Preparation of Polyimide-Cellulose Composite Using Oligoimide with Ethynyl Terminals

Tomoya Shirata, Tatsuki Kon, Keiko Sasaki, Yoshiyuki Oishi, and Yuji Shibasaki^{*} Department of Chemistry and Bioengineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551

(E-mail: yshibasa@iwate-u.ac.jp)

A soluble imide oligomer (IO) (repeating number; 2 and 4) having *N*-phenylated melamine units and phenylethynyl terminals was prepared, and the application to polyimide composites with cellulose (CEL) crystals derived from pulp (CEL_p) or *Halocynthia* (CEL_h) with or without a modifier was investigated. The CEL_h additive up to 0.5 wt % was easily dispersed in IO matrix in solution, and thermostable (glass-transition temperature, ca. 285 °C) transparent tough film (tensile strength, ca. 169 MPa; elongation at break, ca. 8.9%; tensile modulus, ca. 4.6 GPa) was obtained, while the addition of a modifier such as cetyltrimethylammonium bromide and poly(ethylene glycol) derivatives was necessary to obtain a similar tough film for the CEL_p additive.

Polyimides (PIs) have been widely adopted in a variety of fields due to excellent thermal and mechanical properties.¹ Generally speaking, the molding of this type of polymer is difficult because of the high melting point and insolubility in organic solvents arising from the rigid rod structures. Thus, many kinds of processable PIs have been developed so far by introducing amide,² ether,³ and sulfide⁴ functions. These PIs, however, have poor miscibility with carbon or glass fibers, so that the addition of fillers to make higher performance PI composites is relatively difficult. With this view, addition-type PIs have been developed; they are easily processable in the form of short chain oligomers end-capped with latent crosslinking sites.⁵ The TRW's PI resin (P-13N),⁶ that is an imide oligomer end-capped with norbornene moiety, was first introduced. LARC-137 was then developed, which is a thermosetting resin based on 4,4'-diphthalic acid dianhydride, diamine, and norbornene-5,6-dicarboxylic anhydride. The critical issues of these resins are 1) the lower thermostability due to the aliphatic end-group, 2) the need of high-pressure processing in order to suppress retro Diels-Alder reaction, and 3) the use of hightemperature aprotic solvents such as N-methylpyrrolidinone (NMP) to fabricate the polyimide composites. Polymerization of monomeric reactant (PMR)⁸ has been developed, in which low-temperature aprotic solvents such as methanol can be used to immerse monomeric anhydrides and diamines into carbon or glass fibers. The drawback of these PI composites is the need of harsh process conditions and low toughness, which causes abrasion and cracks on the surface of the composites. Yokota and his co-workers developed a high-temperature, processable thermosetting imide resin with good mechanical properties (TriA-PI),⁹ composed of asymmetric imide oligomers and phenylethynyl terminals. The oligo(amic acid) of TriA-PI is dissolved in aprotic solvent, in which carbon or glass fibers are immersed. Thermal curing of this material gives high-performance PI composites, but careful process conditions must be taken in order to obtain homogeneous composites free from an airvoids arising from the water generated during the imidization.



Figure 1. Fabrication of IO–CEL composites. The SEM images show (a) pulp-derived CEL (CEL_p, 1000 nm scale bar) and (b) *Halocynthia*-derived CEL (CEL_h, 100 nm scale bar).

They have also developed a highly soluble imide oligomer (IO) based on 2-phenyl-4,4'-diaminodiphenyl ether. The oligomer shows excellent solubility and was thus applied to a composite with carbon fiber.¹⁰ We have recently reported the synthesis and properties of triazine-containing PIs, which have unusual high solubility in organic solvents along with good mechanical properties.¹¹ Thus, we expected that the IO with a triazine moiety would show adequate solubility in order to fabricate imide composites. As for the additives to fabricate the composite, we chose two types of cellulose crystals, CEL_p and CEL_b, derived from pulp and *Halocynthia*, respectively. The average size and shape of CEL_p are about 50 µm in plate-like crystals, and those of CEL_h are 20 nm wide and 1 mm long nanofibers (Figure 1). Thus, we here report the synthesis of soluble IO with N-phenylated melamine units and phenylethynyl terminals, and the application to PI composites with CEL crystals, which are common bio-macromolecules, and frequently applied as reinforcements for polyolefins.¹² We also expected that the hydroxy groups in CEL could strongly interact with triazine units in IO to afford well-dispersed PI composites.

The phenylethynyl-terminated amic acid oligomer (AAO) was prepared by conventional low-temperature polyaddition of 2,4-bis(4-aminoanilino)-6-anilino-1,3,5-triazine (ATDA),13 ODA, and BPDA in NMP at 10 °C for 1 h, and 60 °C for 4 h, followed by reaction with 4-(phenylethynyl)phthalic anhydride (PEPA) at 20 °C for 12 h (Scheme 1). The resulting AAO solution was cast on a glass plate, and heated at elevated temperature up to 250 °C for 1 h to give the corresponding IO. Two types of IO samples, IO₂ and IO₄, were prepared by changing the feed of anhydride and amine monomers of 2:3 and 4:5, respectively. Table 1 summarizes the results of the oligomerization. Both of the oligomers were successfully obtained in high yields with comparable molecular weights (determined by GPC) to the calculated values, which indicates the oligomers have the expected composition of each monomer. The structures of the IO_x (x = 2 and 4) were characterized by IR (Figure 2) and the elemental analysis. The absorption at $1680 \,\mathrm{cm}^{-1}$



Scheme 1. Synthesis of the phenylethynyl-terminated amic acid oligomer AAO_{xx} and the corresponding IO_{x} .

Table 1. Synthesis of IO_x

Sample	Feed/mol %				Yield ^a	$M_{\rm n} imes 10^{-3}$		11 /11 b	
	ATDA	ODA	BPDA	PEPA	/% Calc	Calcd	Found ^b	$M_{\rm W}/M_{\rm n}$	
IO ₂	1.5	1.5	2	2	87	1.8	1.6	3.1	
IO ₄	2.5	2.5	4	2	77	2.9	3.5	2.1	

^aMethanol-insoluble part. ^bDetermined by GPC (NMP, PSt).



Figure 2. IR spectra of cured amic acid oligomer (AAO) at the set conditions.

corresponding to the amide stretching observed in AAO samples completely disappeared after heating at 250 °C for 1 h, and a new absorption corresponding to imide carbonyl stretching was observed at 1760 and 1710 cm⁻¹, the intensity of which was saturated at 250 °C for 1 h. At 2210 cm⁻¹, the terminal phenylethynyl absorption was observed, whose intensity was almost the same (vs. the intensity of ether absorption at 1235 cm⁻¹) during the imidization reaction. These results supported the satisfactory formation of the IOs with expected structure.

Generally speaking, IOs show poor solubility in organic solvents, however, the prepared IO samples described above are soluble in aprotic solvents such as NMP and DMAc; the oligomers were completely soluble in the solvent at 0.2 wt % at $20 \,^{\circ}\text{C}$, and even at 30 wt % on heating. These results clearly indicated that the anilinotriazine pendent should effectively disturb the strong aggregation between aromatic imide groups, resulting in excellent solubility.

The IO sample was then dissolved in NMP, and 0.5-2 wt % CEL crystals (0.25–1 wt % to IO) dispersed in water was added



Figure 3. IR spectra of (a) as-made IO, (b) hot-pressed IO, (c) hot-pressed mixture of IO with CEL_h , and (d) hot-pressed mixture of IO with CEL_p .

into the solution, and transferred onto a petri dish, followed by the removal of the solvents in a vacuum oven at 250 °C for 12 h. The resulting brown solid was crashed and ground well to afford a IO-CEL mixture. This mixture was hot-pressed at elevated temperature up to 370 °C for 1 h under 3 MPa to afford a brown transparent composite film. The characterization of the composites was performed by IR spectroscopy, in which the characteristic absorption corresponding to ethynyl stretching at 2210 cm⁻¹ almost disappeared after the hot-press process as shown in Figures 3c-3f. The hot-pressed film does not show any solubility in an organic solvent. These results indicated that the ethynyl group at the terminus of the IO sample in the mixture quantitatively reacted to give the composite with the crosslinked structure. In order to characterize the structure of CEL crystals in the composite after hot pressing, the CEL_p crystals were hot-pressed at 370 °C for 1 h under 3 MPa pressure (exactly the same conditions for making the composite film) between two polyimide (Upilex[®]) films. The white powdery CEL_p sample turned into black powder with reducing the weight by 81% from the original. In the IR spectrum of this sample (Figure 3b), the characteristic OH absorption at 3346 cm⁻¹ and aliphatic ether absorption at 1060 cm⁻¹ (Figure 3a) almost disappeared. The elemental analysis of the hot-pressed CEL_p sample shows the content of C, H, and O of 73.63, 3.59, and 22.78%, which is quite far from the original contents of 42.74, 6.17, and 51.09, respectively. Therefore, the mixed CEL components should be within the crosslinked imide matrix as the carbonized structure.

Table 2 shows the thermal properties of the composite films. The glass-transition temperature (T_g) of the crosslinked IO (X-IO) by hot pressing are 282 and 281 °C for X-IO₂ and X-IO₄, respectively. While the composites with the CEL_p additive show similar T_g , CEL_h was effective to provide slightly higher T_g . The small nanofibrous structure was able to disperse well in the polyimide matrix, and thus the mobility of the polymer chain should be restricted as depicted in Figure 1. The formation of composites did not affect the thermal degradation process a lot, but the char yields were somehow increased.

Table 3 summarizes the mechanical properties of the composite films. The brittle property of $X-IO_2$ film was improved with the addition of CEL_h (Runs 1 and 10), while

Table 2. Thermal properties of hot-pressed IO_x and the composites

Dun	Polymer	Cellulose	$T_{\rm g}^{\rm a}$	$T_{\rm d5}/^{\circ}{\rm C}^{\rm b}$		$T_{\rm d10}/^{\circ}\rm C^b$		Char/%	
Kull		/wt %	/°C	in N_2	in air	in N_2	in air	(in N ₂ 800 °C)	
1	X-IO ₂	_	282	473	482	511	531	62	
2	$X-IO_4$	_	281	495	500	526	551	61	
3	X-IO ₂ -CEL _p	0.5	280	486	484	520	532	63	
4	X-IO ₄ -CEL _p	0.25	279	492	501	524	545	63	
5	X-IO ₄ -CEL _p	0.5	280	490	500	521	547	63	
6	X-IO ₄ -CEL _p	1	279	493	504	524	548	65	
7	X-IO2-CELh	0.5	285	475	480	513	531	65	
8	$X\text{-}IO_4\text{-}CEL_h$	0.25	283	488	498	519	538	62	
9	X-IO ₄ -CEL _h	0.5	281	495	503	525	544	65	
10	$X\text{-}IO_4\text{-}CEL_h$	1	285	493	506	525	550	62	

^aDSC (N₂) at a heating rate of 20 °C min⁻¹. ^b5% and 10% weight loss temperatures by TGA in air or nitrogen at a heating rate of 10 °C min⁻¹.

Table 3. Mechanical properties of IO_x and the composites

Run	Polymer	Modifier	Cellulose /wt%	T₅ ^a ∕MPa	E_{b}^{b} /%	$T_{\rm M}^{\ \rm c}$ /GPa
1	X-IO ₂	_	_	61	3.0	4.5
2	$X-IO_4$	—	—	147	4.5	4.8
3	X-IO ₂ -CEL _p	_	0.5	48	2.7	3.5
4	X-IO ₄ -CEL _p	—	0.25	130	4.2	4.3
5	X-IO ₄ -CEL _p	—	0.5	158	4.3	4.6
6	X-IO ₄ -CEL _p	_	1	110	4.2	3.0
7	X-IO ₄ -CEL _p	CTAB ^d	0.5	146	6.8	4.6
8	X-IO ₄ -CEL _p	SDS ^e	0.5	104	4.1	3.9
9	X-IO ₄ -CEL _p	TRITONX-100 ^f	0.5	124	8.9	1.9
10	X-IO2-CELh	_	0.5	79	4.8	4.0
11	X-IO ₄ -CEL _h	—	0.25	129	4.8	4.6
12	X-IO ₄ -CEL _h	—	0.5	169	5.1	4.2
13	X-IO ₄ -CEL _h	—	1	106	3.1	4.4

^aTensile strength. ^bElongation at break. ^cTensile modulus. ^dCetyltrimethylammonium bromide. ^eSodium dodecyl sulfate. ^fPoly-(ethylene glycol) (1,1,3,3-tetrabutyl)phenyl ether.

no significant improvement was observed for CEL_p introduced composites (Run 3). In the case of X-IO₄, the tensile strength (T_s) of the composite film increased with the amount of CEL from 0.25 to 0.5 wt%, but decreased after that. When an over 0.5 wt% of CEL sample was added to the IO solution, the appearance of the finally obtained film became inhomogeneous. This could be attributed to the large phase separation between IO solution in NMP and CEL dispersion in water. However, it is clear that CEL_h should be the better choice as an additive because the higher T_s of 169 MPa and higher elongation at break (E_b) of 5.1% were achieved. Again, this can be explained by the size and the shape effect of the nanofibrous CEL_h nature.

In order to improve the mechanical properties of X-IO₄-CEL_p composites, we then used several surfactants as the modifier. As shown in Table 3, among them, cetyltrimethylammonium bromide (CTAB) and poly(ethylene glycol) (1,1,3,3-tetramethylbutyl)phenyl ether (TRITONX-100[®]) realized higher elongation at break up to 8.9% for the X-IO₄-CEL_p composite film. The cationic surfactant could get good interaction with melamine moiety, and link with aliphatic CEL molecules very well.

In conclusion, we successfully prepared an IO sample bearing N-phenylated melamine units and phenylethynyl terminals, and achieved excellent solubility in aprotic solvents. The imidization was performed in a conventional thermal process ate elevated temperature up to 250 °C. The composite formation was performed by mixing IO with CEL in NMP/water medium, and the dried solid was well ground in a mortar, and hot pressed at 370 °C for 1 h under 3 MPa pressure. The quantitative reaction of the terminal ethynyl group was confirmed by IR, and the introduced CEL was found to change into the carbonized state by IR and elemental analysis. The composites show slightly higher $T_{\rm g}$ (≈ 285 °C), char yields (ca. 65%), and much better mechanical properties ($T_{\rm s} \approx 169 \,\text{MPa}$, $E_{\rm b} \approx 8.9\%$). When the two CEL additives were compared, CEL_h from Halocynthia showed better results in view of the thermal and mechanical properties. This can be explained by the size and the shape of the nanofibrous CEL_h characters. CEL_p, a more common material, can show similar improvement for IO resin when the additional modifier is applied for composite formation.¹⁴

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